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Quantitative Emission Spectrum Analysis. IV
Determination of the Silica Lime Ratio in Basic Slag*

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Synopsis

A rapid and accurate determination of the ratio of lime and silica in basic slags was carried out by the spectrum method. In the present method, the powdered sample is placed in a concave of copper electrode without using any adhesive agent, and the emission is made against the same typed second electrode without any preliminary discharge. And the dry plate is treated with methanol after washing to shorten the analytical time. By this method it is possible to determine 2-4 of the ratio of lime and silica in basic slags within about one hour and with errors less than 10%.

I. Introduction

It is the most important matter in the open-hearth work to know quickly and accurately the ratio of lime and silica (CaO/SiO_2) in the basic slag. When the spectrum method is employed for the purpose, it is much quicker to seek directly the logarithm of the ratio of lime and silica from the calibration curve than to determine the quantity of each of them and then seek the ratio. The former method was already attempted by R.H. Steinberg and others(1), who used pure-carbon electrodes as the auxiliary electrodes and put powdered test materials dribbled with 2% Ethocel buthyl acetate solution in it, and, after drying, photographed it. However, auxiliary electrodes made of carbon are rather expensive and consumytive. So, the author has studied various types of non-consuming electrode and moreover, performed experiments under various emission conditions of powdered test materials, fluid, half-dried, and dry solid forms. J. Eeckhout(2) made the emission on a plate of graphite using cupric oxide as an internal standard.

The equipments used were, same as in the previous report(3), Qu 24 type quartz spectrograph, Feusner type generator and microphotometer. The test materials used in this experiment were those offered by the Yawata Steel Works of Japan Steel Company, and also the materials symthesized by adding silica and lime to them.

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* The 598th report of the Research Institute for Iron, Steel and Other Metals.

(1) R. H. Steinberg and H. J. Belic, Anal. Chem, 20 (1948), 72.
(2) J. Eeckhout, Spectro. Chim. Acta, 3 (1949), 575. C.A. 43 (1949), 8307.
(3) S. Musha, J. Japan Institute of Metals, 12 2-3 (1948), 37

II. Experimental procedure

1. The preparation of test materials

The samples, No. 48, 49, 51 and 52 of the Technological Laboratory of the Yawata Steel Works, are heated in a porcelain crucible for one and a half hours at 900°C, after cooling, ground into fine powder in an agate mortar, and passed through a copper sieve of 80 meshes. These samples had more blackness than before the heating, and their basicity also changed; namely, their lime/silica ratios were 2.912, 4.208, 2.687, and 3.710 respectively before the heating, but they went down to 2.689, 3.713, 2.630 and 3.499 after the heating. The analytical values of the samples were determined in the following procedure: Dissolve 0.2-0.3 g of the powdered sample in aqua regia, add 60% $HClO_4$, concentrate until it produces

Table 1.

	Artificial samples			Actual samples			
	G-2′	G-3′	G-6′	S-48′	S-49′	S-51′	S-52′
Sample taken(g)	0.1911	0.2046	0.1852	0.2001	0.2016	0.1969	0.2063
SiO_2(1) found	0.0336	0.0298	0.0218	0.0317	0.0247	0.0311	0.0265
SiO_2(%)found	18.21	14.57	11.77	15.84	12.25	15.79	12.85
0.1045N-$KMnO_4$ titre. (ml)	24.75	30.03	30.90	29.38	31.59	28.20	31.95
CaO(%) found	38.69	42.58	47.69	42.59	45.48	41.52	44.96
CaO/SiO_2	2.125	2.922	4.052	2.689	3.713	2.630	3.499
log CaO/SiO_2	0.327	0.466	0.608	0.430	0.570	0.420	0.544

white fumes of $HClO_4$ and filter the dehydrated silicic acid and then determine lime and silica by the usual method. The results of the analyses are shown in Table 1. The samples after the heating are illustrated by a mark ′ in the table.

2. The synthesis of test materials

In order to make the artificial sample similar in its property, CaO or SiO_2 was added as little as possible to the actual samples, which is nearest to the desired CaO/SiO_2 value and they were mixed well in an agate mortar. Then it was heated in a porcelain crucible for one and a half hours at 900°C in the same manner as above, ground into fine powder and then passed through a copper sieve of 80 meshes.

G-2′ is a mixture of 4.8 g of S-51 and 0.2 g of SiO_2. G-3′ is a mixture of S-54, S-55 and S-56 in the proportion of 2:1:1, and its lime/silica ratio is 2.800 before heating and 2.922 after heating. G-6′ is a mixture of 4.5 g of S-49 and 0.5 g of CaO, and treated in the same way as above. The analytical results of these artificial test materials by the same method are shown in Table 1.

3. Reagents

SiO_2: About 24 g of extra pure sodium silicate was dissolved in 100 ml of water, and 20 ml of concentrated sulphuric acid was added to it. The solution was then evaporated almost to dryness, and then water was added and it was boiled. It was then washed several times by decantation until no SO_4'' was detected in the solution. The precipitate of silica thus obtained was filtered off and heated

in a porce'ain crucible at 900°C for about two hours, and then ground into fine powder in an agate mortar.

CaO: Extra pure CaO was heated at 900°C for two hours and ground into powder.

Sucrose solution: Crystal sucrose was recrystalized once with water and ethyl alcohol, and its 33% aqueous solution or the same one containing 0.1 N HCl was used.

Polystirol solution: Two per cent polystirol amylacetate or butylacetate solution was used.

4. Emission conditions of samples

It is extremely difficult to obtain the quantitative conditions of the emission of powdered samples. The author, therefore, attempted to let them discharge in a

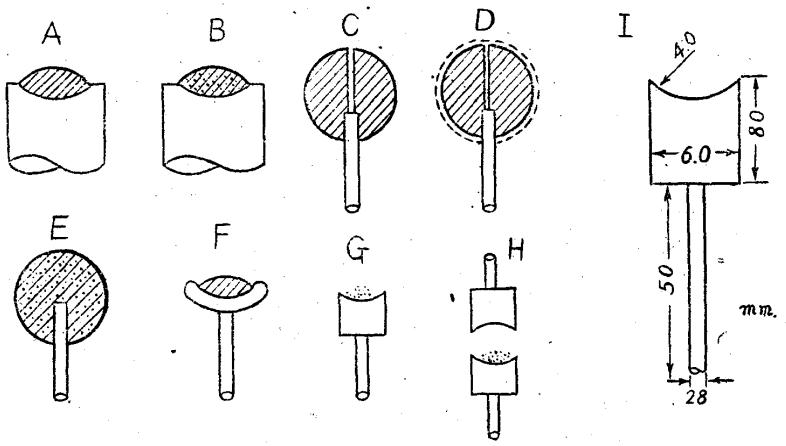

Fig .1

state, kneaded or moistened with sucrose solution or polystirol solution, and performed experiments with various kinds of electrodes as shown in Fig. 1.

As the secondary electrode of A to G, a rod-shaped conical end electrode made of pure copper was used, but in H, two same typed electrodes were set against each other.

As the adhesive agent, the author used sucrose solution, polystirol and a syrup consisting of phosphoric and hydrofluoric acids. The slags adhered with these agents have unexpectedly a high electric resistance. For instance, A type using sucrose as an adhesive agent showed several megohms in the dry state. Consequently, with A type, the sparks crept along the surface of the samples, and took place only against the copper electrodes and not directly against the sample. A little improvement was seen in a similar experiment with B, which was made to contain 10% pure copper powder as an attempt to obtain better results. C, D, and E were moulded at an end of a copper rod of 3 mm in diameter with the above mentioned various adhesive agents. Over the surface of D some copper powder was dusted uniformly. E is moulded with the test materials containing 10% copper powder. F is a copper rod with a concave copper plate. The electrodes shown in G and H are improved ones of the above. G and H are a copper cylinder 6 mm in diameter and 8 mm in length with a concave 4 mm in

curvature radius at one end, and a brass rod 2.8 mm in diameter and 50 mm in length as shown in detail in I of Fig. 1. Photographs were taken using various electrodes mentioned above, and the line pair of Ca 2791.6 Å/Si 2881.6 Å was employed and its blackness was measured. The results obtained showed that the sparks with A, B, C, and E types were unstable and unquantitative, and with D, F, and G the sparks became somewhat stable, but these were not practical. As an example, the experiment with D type is shown in Fig. 2. With H, the sparks

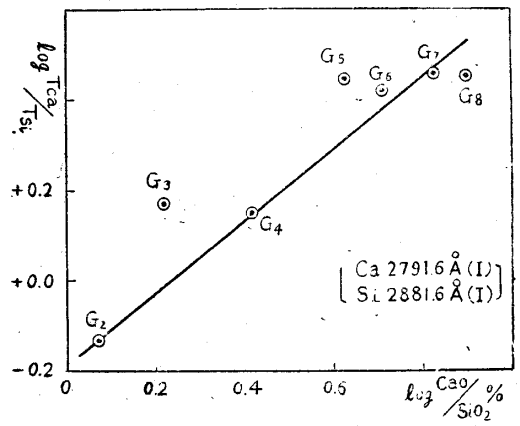

Fig. 2

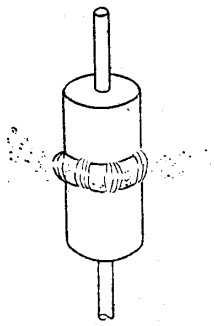

Fig. 3

danced around the outside as shown in Fig. 3, which showed the effect of making uniform and decreasing the exodus of powder. The time required for the complete exodus of powder was 35 seconds in the average of 20 experiments. Therefore, the H type was used, and the powder was left to emit without using any adhesive agent. However, when the conical end electrodes are used as the secondary one of F and G, the above method is not applicable as the sample will be immediately flied away by the sparking flash.

5. Photographing conditions

The spectrum line of Si does not appear very clearly by the sparking method. On the other hand, Ca is easily excited because it is an alkaline earth, and the line of Ca to be set against 2881.6Å or 2516.6Å of Si can not be found, and no line of Si appears near Ca. The author was consequently obliged to choose Ca 4318.7Å (I)/Si 2881.6Å (I) as the line pair.

The photographing conditions were determined as shown in Table 2, after various preliminary experiments.

Table 2.

Primary voltage	100-0.5V
Primary current	3.1-0.05A
Slit width	4/100mm
L=0.0829 mH	C=0.020/F
Electrode distance	2.5mm
Exposure	30 seconds
Fuji process hard dry-plate	
Development : FDNo. 31, at 18°C, 3min	

6. Analytical procedure

Powdered sample on a very small spatula is put on the electrode shown at I of Fig. 1, and spread uniformly along the surface with the handle of the spatula. A same typed electrode as the secondary is set against it at a distance of 2.5 mm. Exposure is made directly for 30 seconds without performing any preliminary discharge. More than 10 electrodes are prepared, and photographs are taken

successively one after another. The time required for photographing one test material is about 50–60 seconds. The surface of the electrodes must be polished after each discharge, to enable the sparks to dance well.

7. Rapid treatment of dry plates

As a method for the rapid treatment of dry plates after the photographing, Steinberg and others treated it with the Kodack rapid liquid fixer, then washed for one minute, and dried with infra-red ray. However, the author, in this experiment, did one-minute washing after fixing for 3 minutes, dipped it immediately for one minute in methanol and then dried in an air dryer at 40–45° C for 2–3 minutes. By this method, it is about 10–11 minutes from the development to drying. Moreover, to ascertain effects what this treatment has upon the blackness, an experiment was performed as follows: the dry plate was divided into upper and lower portions, in parallel with its long axis and the upper portion alone was given a medium exposure. That one portion of the dry plate was rapidly treated and the other was ordinarily treated and the difference was calculated by measuring the blackness. The results are shown in Table 3.

Table 3.

	Ordinarily treated plate		Rapidly treated plates	
	Exposed part	Unexposed part	Exposed part	Unexposed part
Error in mean square (%)	0.98	1.40	2.44	3.24
Average (%)	1.19		2.84	

The blackness was measured of four dry plates, at 15 points on each of the upper exposed and the lower unexposed parts. Starting from a point 15 mm from the upper edge and 70 mm from the left edge of the plates, 15 points were taken at a distance of 3 mm in the upper portion, and starting from a point 10 mm from the low edge and 70 mm from the left, 15 points were also taken in the lower portion. As it is clear from Table 2, the increase of the mean square error by this treatment is 1.65% in an average of the exposed and the non-exposed parts. This increase of the error was considered due to an unbalanced distribution of salts resultant from an imperfect elimination of developing and fixing solutions,

Table 4.

Samples	Ca 4318.7Å T(average)	Si 2881.1Å T(average)	TCa/Tsi	log TCa/Tsi	Standard sample log CaO/SiO_2	Found CaO/SiO_2
G–2	331.0	100.0	3.310	0.520	0.327	– –
G–3	465.5	182.0	2.557	0.408	0.466	– –
48	358.5	132.0	2.716	0.434	– –	0.425
49	326.0	165.0	1.976	0.296	– –	0.570
G–6	380.0	209.0	1.818	0.260	0.608	– –

and to an unbalanced coagulation of the gelatine due to methanol.

III. Results of experiment and considerations

Table 4 and Fig. 4 show one of the analytical results by the photographing done under the conditions determined by the above-mentioned various preliminary experiments, and of the quantitative determination by a comparison method. Table 5 shows the overall results of the analysis. Thus it is possible to determine 2-4 of the lime/silica ratio in the basic slag.

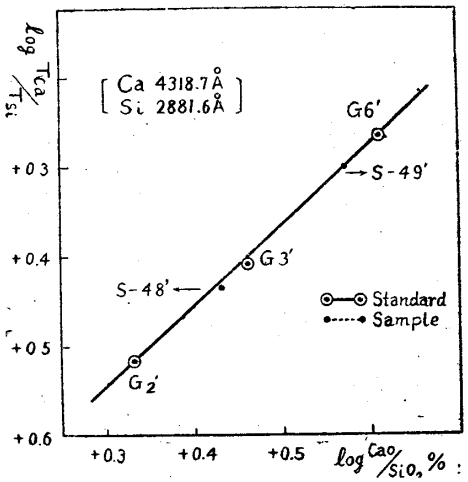

Fig 4.

In this emission method, it often happens that the sparks do not dance and a stationary discharge occurs, or it follows an error due to a short period of the exposure and unexpected errors due to non-uniformity of the samples on the electrode. The values of such errors were put out of consideration, but should be less than 10%.

Table 5.

Samples	CaO/SiO_2											
	S—48′			S—49′			S—51′			S—52′		
	log	CaO/SiO_2	Difference	log	CaO/SiO_2	Difference	log	CaO/SiO_2	Difference	log	CaO/SiO_2	Difference
Spectrum method	0.425	2.66	−0.03	0.570	3.71	±0.0	0.420	2.63	±0.0	0.543	3.49	−0.01
	0.428	2.68	−0.01	0.565	3.67	−0.04	0.410	2.57	−0.06	0.539	3.46	−0.04
	0.430	2.69	±0.0	0.570	3.71	±0.0	0.401	2.52	−0.11	0.497	3.14	−0.36
	0.425	2.66	−0.03	0.560	3.63	−0.08	0.353	2.25	−0.38	0.503	3.18	−0.32
	0.437	2.74	+0·05	0.566	3.68	−0.03	0.422	2.64	+0.01	0.539	3.46	−0.04
	0.447	2.80	+0.11	0.563	3.66	−0.05	0.403	2.53	−0.10	0.553	3.57	+00.7
Chemical method	0.430	2.689		0.570	3.713		0.420	2.630		0.544	3.499	

Table 6.

Procedure	Time required (min)
Photographing of samples	7
Development	3
Fixing	3
Washing	1
Methanol treatment	1
Drying	3
Measurement of blackness	15—20
Calculation	15—20
Total	48—58

The time required for the analysis is about one hour, as shown in Table 6, per one dry plate, on which photographs of 3 standards and 4 test materials are

taken and which is rapidly treated.

Summary

The present study was carried out for the rapid and accurate estimation of the ratio of lime and silica in basic slags by the spectrum method, which was an important matter in the open-hearth work.

(1) Emission of samples were made under various conditions and the most successful one was decided as follows. Electrode was one made of copper, which was consisted of a 6×8 mm cylinder and a brass 2.8×50 mm rod, and had a concave of 4 mm curvature radius at an end. Powdered sample of 80 meshes was placed in the concave of the electrode without using any adhesive agent.

(2) The discharge was made against the same typed second electrode placed at a distance of 2.5 mm. Exposure was made directly for 30 seconds without performing any preliminary discharge.

(3) Dry plate were treated with methanol for one minute after washing and dried in an air dryer at 40-45° C for 2-3 minutes.

(4) Ca 4318.7 Å (I)/Si 2831.6 Å (I) was chosen as the line pair and by measuring blackness of it, 2-4 of the lime/silica ratio was determined with errors less than 10 % and within one hour.

In conclusion, the author expresses his deepest gratitude to Prof. H. Gotô for his kind guidance, and also offers his best thanks to Mr. T. Ôtsuki who helped the author in his experiments.